Final Technical Report

Student Support for Chemical Interdiffusion Studies
at Pseudomorphic Interfaces

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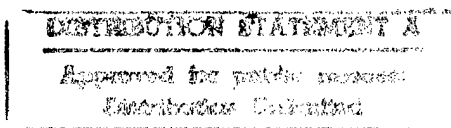
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Uncertainty in the extent of solid solution formation in the SiC-AlN system has continued to exist for temperatures $< 2000°$ C. This uncertainty has been surmounted via chemical interdiffusion investigations between epitaxial, monocrystalline 2H-AlN(0001) films and their associated 6H-SiC(0001) substrates between 1700° and 1850°C. The characterization tools of Auger spectroscopy, transmission electron microscopy, and parallel electron energy loss spectroscopy have been employed to determine the diffusion profiles across the AlN/SiC interfaces. This research has found no evidence of interdiffusion between AlN and SiC and thus proven that pure AlN and SiC do not form measurable solid solutions below 1850° C.

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A. Introduction

Interest in wide bandgap semiconductors for high-temperature and high-power electronic and short-wavelength optoelectronic applications has increased substantially in the past decade. Silicon carbide and aluminum nitride are two of the most important materials in this group. The former occurs in a large number of polytypes or Si/C bilayer stacking arrangements along the direction of closest packing. The most common of these polytypes are the hexagonal polytypes of 6H and 4H and the cubic zincblende 3C polytype, where the number refers to the number of bilayers necessary to produce a unit cell and the letter refers to the basic crystal symmetry of this cell.

Silicon carbide (SiC) has long been of interest because of its superior structural, thermal and electrical properties. High temperature and/or erosion- and corrosion-resistant wear parts, as well as optoelectronic and microelectronic semiconductor devices, are representative applications. Control of the physical and chemical properties of SiC via microstructural changes achieved by using different processing routes has been extensively studied for many years. The microstructural variables most frequently altered include the amount and the morphology of the various polytypes in the processed material, intentionally introduced, non-boundary, second and additional phases and additions of sintering aids which may or may not form a grain boundary phase. The processing temperature, impurity content, and sintering (or annealing) atmosphere affect the resultant microstructure. However, the primary material remains SiC. Another approach to property engineering involves the alloying of SiC with other ceramic compounds to alter, e.g., the band gap. This approach has also been of interest for several years, and the determination of the extent, if any, of alloying in the SiC-AlN system was one of the primary objectives of this research program.

One compound which has been reportedly alloyed with α(6H)-SiC ($a_0 = 3.08$Å) is AlN ($a_0 = 3.11$Å) due to the similarities in the covalent radii and the crystal structures. Aluminum nitride has considerable potential for use with SiC or, more likely, GaN and InN to produce light emitting and laser diodes in the ultraviolet region due to its large and direct band gap. It typically forms in the wurtzite (2H) structure. The electronic properties for pure AlN are not as well known as, e.g., 6H-SiC due to its high resistivity, relative difficulty of formation in single crystal boule form and the ease of oxygen incorporation during growth. The results of theoretical calculations have been used to predict the occurrence of solid solutions between AlN and SiC, the regions of immiscibility and the nature of the band-to-band transitions as a function of composition in this binary system. Experimental research involving diverse processing routes has also been conducted in ceramic systems. The results are not in agreement regarding the solubility, but tend to show that some solubility is possible, especially at temperatures above 2000°C. Thin film growth research under non-equilibrium conditions more commonly shows that partial or complete solid solutions from these two compounds can be

achieved; however, whether or not phase separation would occur upon heating has not been studied. A critical review of this research is provided.

The primary objective of this research was the determination of the degree, if any, of chemical interdiffusion between monocrystalline AlN and SiC at elevated temperatures and, therefore, the veracity of the various phase diagrams which have been published for this system. The following paragraphs present a description of the experimental procedures employed in this research, an analysis and discussion of the results obtained, and the major conclusions drawn from these results.

B. Experimental Procedure

Sample Preparation. Diffusion couples composed of single crystal, vicinal 6H-SiC(0001) wafers cut off-axis 3°- 4° toward [1120] and monocrystalline AlN(0001) films with low concentrations of planar defects were prepared in a modified Perkin-Elmer 430 gas source molecular beam epitaxy (GSMBE) system. Prior to loading into the GSMBE chamber, the SiC wafers were dipped into 10% HF to remove as much SiO_2 as possible, rinsed in distilled H_2O, placed onto the heating stage contained in the transfer tube of the GSMBE system, thermally desorbed at 750°C for one hour and moved into the GSMBE chamber. This desorption step removed essentially all the remaining oxygen and all of the carbon still adsorbed to the surface. Ultra-high vacuum conditions in the transfer tube insured that little reoxidation or contamination of the surface would occur before the initiation of film deposition.

Aluminum (99.999%) was evaporated from a standard effusion cell. Activated nitrogen was achieved using an MBE compatible, electron cyclotron resonance (ECR) plasma source. Growth conditions for the films are presented in Table I. Several different precautions were taken in order to prevent contamination of the samples and to minimize the loss of volatile components principally aluminum, and nitrogen. The samples were placed in a high density pyrolitic graphite crucible. The inside of each crucible was previously coated with SiC by heating a mixture of Si and β-SiC inside the enclosed holder to 2000° C for 4 hr. The diffusion samples were placed inside this holder with the α(6H)-SiC[0001] face against the SiC coating. Bulk AlN squares were placed on top of the deposited AlN. The holder was subsequently closed using a threaded lid and loaded into a W element vacuum furnace. The chamber was evacuated (2×10^{-6} Torr) to prevent contamination during diffusion. Nitrogen gas (99.9995%), further purified through a gettering furnace containing Cu chips heated to 850°C (Centorr Furnace model 2B-20), was then introduced into the chamber at a rate of 365 sccm which was controlled by a mass flow meter (MFC). The chamber was brought to atmospheric pressure and a flowing N_2 environment maintained throughout each diffusion anneal. Diffusion temperatures were reached in ≈ 20 min (exact value for 1850° C). The temperature of the

Table I. Growth Conditions for the 2H AlN Films on α(6H)-SiC(0001) Substrates

Chamber base pressure	4×10^{-10} Torr
Chamber operating pressure	5×10^{-4} Torr
Nitrogen pressure	2×10^{-4} Torr
Nitrogen flow rate	4-5 sccm
ECR microwave power	50 W
Substrate temperature	650° C
Growth rate	≈0.1 mm/hr
Total growth time	7-8 hrs.

furnace was controlled using an optical pyrometer and a feedback and control loop to the power supply. The samples were then removed for characterization. The N_2 gas, bulk AlN, and SiC coated crucible are not meant to aid in the diffusion. This was checked by a SiC-AlN standard which had not been annealed. The AlN and the SiC intensities in the standard were the same as the AlN and SiC intensities outside the diffused region. The samples were annealed within a temperature range of 1700°C–1850°C for times ranging from 10h–50h. A complete listing of temperatures and times are given in Table II.

Table II. Annealing Conditions used for the AlN/SiC Diffusion Couples

Temperature (°C)	Time (hrs)
1700	30
1700	70
1750	25
1750	50
1750	70
1800	20
1800	25
1800	30
1850	10
1850	21.5
1850	25
1850	50

The extent of the chemical interdiffusion within selected AlN/SiC couples was determined using both Auger electron spectroscopy (AES) and cross-sectional analytical and high resolution transmission electron microscopy (AEM and HRTEM) in tandem with parallel-detection electron energy loss spectroscopy (PEELS) equipment. Descriptions of this equipment and the modes of operation for this research are described in the following two subsections.

Characterization: Auger Spectroscopy. The AES studies were conducted in the Oak Ridge Center for Manufacturing Technology's, Testing and Evaluation Center. A Perkin-Elmer Model 660 Scanning Auger Microprobe (SAM) having a cylindrical mirror analyzer (CMA) with a coaxially mounted LaB_6 electron gun was employed. To generate depth profiles, a rastered and focused microbeam of Ar ions with a nominal current of 275 nA was used to sputter away material within a 250×250 um area. Each sample was tilted 30° from the electron-beam normal to furnish an incidence angle of 45° for the ion beam and to minimize charging. The analysis electron beam sampled the central portion (20×20 um) of the much larger sputtered crater. In alternating intervals with ion bombardment, multiplexed energy spectra were acquired for the KLL Auger electron transitions of elements.

The sample geometry and the ion energy in the AES result in an interface resolution of approximately 5-15 nm. The interface resolution is predicted from measurements on known targets and varies depending upon the reference for similar conditions. Among other factors, the interface resolution depends upon sample parameters, the atomic sharpness of the interface, ion beam parameters and sputtered depth. Due to the amount of sputtering needed to reach the interface, an interface resolution near 15 nm is expected.

To quantify the AES sputtering rate, a depth profile was acquired while sampling multiplexed Auger peaks at coarse time intervals. A second depth profile was acquired on a fresh area of the surface. The Auger peaks were sampled at finer time intervals as the interface was approached. Atomic concentration was deduced from the peak-to-peak Auger signals.

At the first indication of the substrate, the time interval was further reduced. A diamond stylus profilometer was used to determine the depth of the sputtered crater. A conversion from sputtering time to depth was calculated assuming that the sputter rate was linear with time. During sputtering within the interface region, the sputtered depth between measurements was calculated to be about 6 nm. This value is near the lower limit on the interface resolution.

Sputter rate standards also served as standards for the 100% intensity peaks for Al, N, Si, and C from which relative concentrations were obtained. The method of two standard deviations in the Gaussian resolution function at the interface was used to specify the width of the interface with the beginning at 84% and the end at 16% signal intensity.

Transmission Electron Microscopy and Parallel-detection Electron Energy Loss Spectroscopy. Each sample was cut into 3 um wide and 500 um thick discs which were

mechanically thinned to ≈100 um and dimpled at the SiC-AlN interface to a final thickness of 20 um. Further thinning of the samples with an ion miller achieved an electron transparent area. An acceleration voltage of 6 kV for initial milling was used; it was decreased to 4 kV for the final milling. The milling angles of 15°, 12°, and 6° were used in sequence during the milling to reduce interface damage. The HRTEM studies were conducted using a Topcon EM-002B instrument at 200kV at NCSU and a Philips CM12 and a CM30 instrument at the Metals and Ceramics Division of the Oak Ridge National Laboratory. High-spatial-resolution parallel-detection electron energy loss spectroscopy used to obtain chemical information from the region near and across the interface of selected samples as well as regions outside the interface area. This study was performed at 100 kV with a Philips EM400T electron microscope equipped with a field emission gun and a Gatan 666 spectrometer. Specimens were cooled to -130°C in Gatan cooling holders to prevent evaporation under the electron beam. Spectra were acquired with probes of 20 Å diameter (FWTM), ≈1 nA, and incident and collection half-angles of 8 and 19 (or 30) mrad.

C. Results and Discussion

The cross-sectional TEM studies stacking faults parallel to the interface, as well as the large step structures on the surface which have resulted from step bunching during growth and numerous threading dislocations running perpendicular to the interface. Thus, although the AlN films were technically monocrystalline in nature, numerous line and planar defects are introduced during growth which could affect the rates of any chemical interdiffusion which may occur. The height of the surface steps formed as a result of step bunching increased from <100 Å in the as-deposited state to within the range of 500 to >1000 Å during the diffusion anneals.

The total Auger depth profile at 1700°C was more than three times that of the unanneled sample, as shown in Table III. However, it is still only ≈380 Å which is definitely within the error of the ability to profile an interface of a sample with an ion beam even rotating the sample. A more telling point regarding the existence of chemical interdiffusion was the much longer total profile in the sample annealed at 1850°C for 25 hr; however, the profile distances for the samples annealed at this temperature and at 1950°C for 50 hr were approximately the same as that determined at 1700°C. This variation of depth profile distances cannot be correlated with temperature or time at temperature and except for the 1850°C - 25 hour sample are essentially the same and, as just noted, within the error normally associated with Auger depth profiles of interfaces.

Because of the uncertainties surrounding the Auger data, subsequent research involved the use of TEM and PEELS in order to employ a very small diameter beam (20 Å) and visual observation to quantitatively examine the interface region of the annealed samples.

Table III. Total Auger Depth Profile

Anneal Temperature (°C) and Time (hr.)	Average Total Profile Distance (Å)
Unannealed	110
1700 - 70	380
1850 - 25	1300
1850 - 50	400
1900 - 50	500

From Auger depth profiles, the interface region (16 nm) of Sample 1 is slightly sharper than the interface region (29 nm) of Sample 3. However, these values are roughly equal to the interface resolution predicted from experimental conditions (15 nm) and are consistent with a well-defined interface.

PEELS chemical analysis of the region around the interface verified that no long range diffusion occurred in samples annealed at 1700°C–1950°C. The smoothness of the concentration verses distance profiles indicated that there were no two phase regions formed in samples annealed between 1700°C–1950°C. This supports the phase diagram presented by Zangvil Ruh that solid solution of AlN/SiC do not occur under 2000°C.

D. Conclusions

Chemical interdiffusion investigations have been conducted between epitaxial, monocrystalline 2H-AlN(0001) films and their associated (6H)-SiC(0001) substrates between 1700° and 1850°C. The characterization tools of Auger spectroscopy, transmission electron microscopy, and parallel electron energy loss spectroscopy were employed to determine the diffusion profiles across the AlN/SiC interfaces. No evidence of interdiffusion between AlN and SiC was observed. Thus pure AlN and SiC do not form measurable solid solutions below 1850°C.